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Effect of Pressure on Mesomorphic Transitions in Cholesterol Esters of Unsaturated C_{18} Aliphatic Acids

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The smectic to cholesteric, cholesteric to isotropic liquid, and solid to isotropic liquid transitions in the following cholesterol esters are determined by an optical method as a function of pressure up to 1 kbar; cholesteryl oleate, cholesteryl linoleate, and cholesteryl linolenate. The pressure dependence of the transition temperatures ($\mathrm{d}T/\mathrm{d}P$) is in the range of 21 to 36 K kbar^{-1}, and the volume changes (ΔV) computed by means of Clapeyron's equation are between 0.42 and 1.3 cm^3 mol^{-1} at 1 bar. The volume change for the smectic to cholesteric transition increases with the number of the double bonds in the acids, while that for the cholesteric to isotropic liquid is little affected by the double bonds.

A study of the effect of pressure on the phase behaviors of liquid-crystal forming materials was begun by Hulett[1)] just 10 years after the discovery of liquid crystals.[2,3)] Similar kinds of work were undertaken by Puschin and Grebenshchikov[4)] and by Robberecht[5)] in the former half of this century. Researches of liquid crystals at high pressure revived one decade ago, and recently developed in various ways with the aid of more advanced techniques for measurements, as briefly reviewed elsewhere.[6)] A useful optical method for detecting mesomorphic transitions at high pressure was invented and applied to cholesteryl stearate in a previous paper.[6)] Cholesterol esters of a homologous series of unsaturated C_{18} aliphatic acids are investigated in the present work. Hydrocarbon chains in the cholesterol esters of saturated aliphatic acids are stretched in the solid(So), smectic(Sm), and cholesteric(Ch) phases and in the isotropic liquid(IL) phase near the Ch–IL transition; all the conformations are in the *S-trans* form.[7)] The conformation about a double bond is considered to be *cis* in the acids studied here.[8,9)] Thus, it is interesting to see how the deviation from the linear conformation (rod-likeness) influences the phase behaviors and volume changes associated with the phase transitions.

Experimental

Cholesteryl oleate(CO), cholesteryl linoleate(CL), and cholesteryl linolenate(CLN) were obtained from Eastman Kodak. The esters were recrystallized from 1-pentanol, washed by a water-ethanol mixture (50 v/v%) and by water, and dried before use *in vacuo* for more than 10 h. As seen in Table 1, the transition temperatures at 1 bar (1 bar$=10^5$ Pa) of the purified materials agree well with the literature values[9)] except for CLN.

The transition temperatures were determined by using an apparatus designed previously in which a He–Ne gas laser (wavelength 632.8 nm and power 3 mW) and a phototransistor were used as a source and a detector, respectively. Pressure was measured to ± 1 bar by a Heise Bourdon gage, and temperature to ± 0.1 °C by a chromel-alumel thermocouple fixed in the high-pressure optical cell. The transition temperatures were reproducible within ± 0.5 °C under any condition. The high-pressure apparatus and experimental procedure were described in detail elsewhere.[6)]

Results and Discussion

A typical example of the transparency variation below and above the Sm–Ch transition is shown in Fig. 1; the transparency increases slightly with increasing temperature in the smectic phase, drops at the transition, and increases more rapidly in the cholesteric phase. The transparency minimum is reported also for the mesomorphic transition in other liquid crystals.[10–12)] Causes for the appearance of the minimum would be strong light scattering and reflection at the boundaries of optically anisotropic domains being reorganized to form the cholesteric order. The positional order in the direction normal to the smectic layer is lost during the smectic to cholesteric transition. Thus, the diffusive motion of a molecule in this direction has something to do with the rate of the transparency drop. The manner how the transparency rose with time (cooling) from the minimum to its

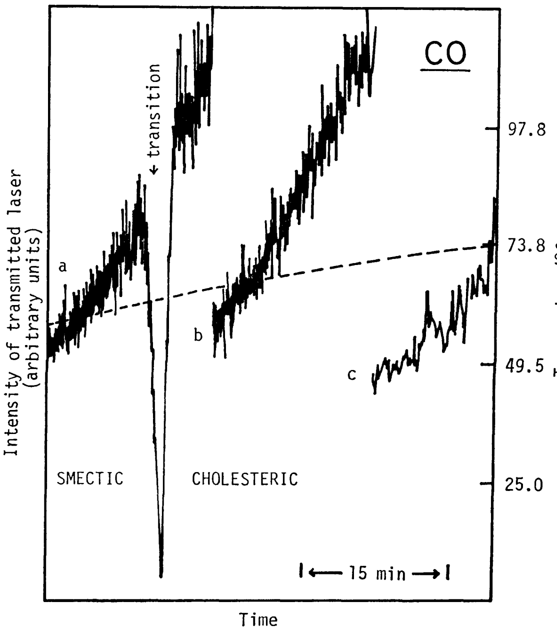

Fig. 1. Optically detected smectic–cholesteric transition in cholesteryl oleate at 920 bar.
—: Intensity of transmitted laser; --: temperature; sensitivity of detecting system, a/c=5 and b/c=2.5.

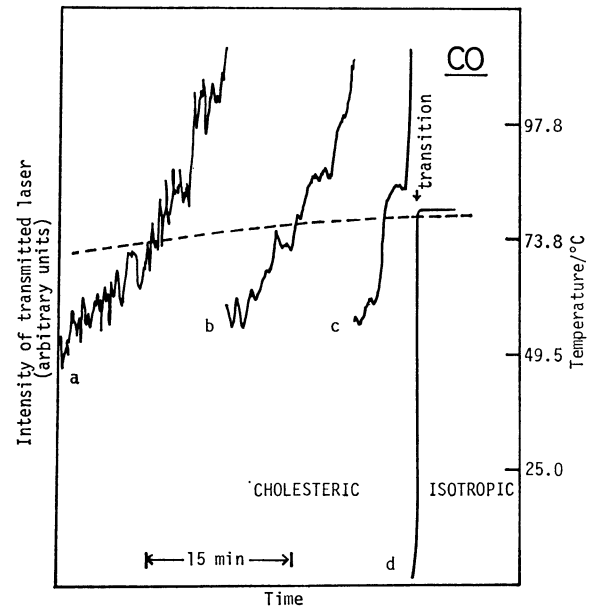

Fig. 2. Optically detected cholesteric-isotropic liquid transition in cholesteryl oleate at 1 kbar.
—: Intensity of transmitted laser; --: temperature; sensitivity of detecting system, a/d=400, b/d=200, and c/d=100.

smectic value was taken as a criterion to judge a tricritical point of the Ch–Sm transition in cholesteryl oleyl carbonate.[12] No corresponding phenomena were observed in these esters at any pressure. Taschek and Williams[13] ascribed the transparency increase with temperature in liquid crystals to the decrease in the birefringent factor, the square of the difference between ordinary and extraordinary indices. Changes in the size of domains and in the pitch of the helical structure in the cholesteric phase would also contribute to the transparency increase. These factors cause the transparency jump finally at the Ch–IL transition, as seen in Fig. 2. Similar changes in transparency took place when material densities were decreased by reducing pressure at almost constant temperature. The transitions in these esters are monotropic with respect to the solid state as,

$$\begin{tikzcd} \text{So} \arrow[rrr, bend right] & \text{Sm} \arrow[l] \arrow[r, leftrightarrow] & \text{Ch} \arrow[r, leftrightarrow] & \text{IL} \end{tikzcd} .$$

The So←Sm transition could not be detected by the present method. The smectic phase of CO and CLN were apt to be supercooled below 0 °C, so that their So→IL transitions were not examined. The absolute value of the transparency in the smectic or cholesteric phase differed from one to another run, especially depending on the cooling rate.

The transition temperatures determined thus are plotted against pressure in Figs. 3, 4, and 5. In Fig. 4, the liquid crystalline phases look as if they were supercooled. Every boundary line in the phase diagrams is straight under the present experimental conditions. The values of the slopes (dT/dP) for the transitions are summarized together with other transition parameters at 1 bar in Table 1. In each ester, the larger the slope the higher the transition point;

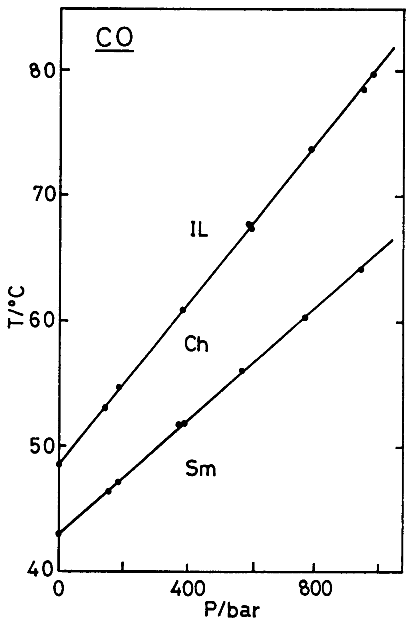

Fig. 3. Phase diagram of cholesteryl oleate.

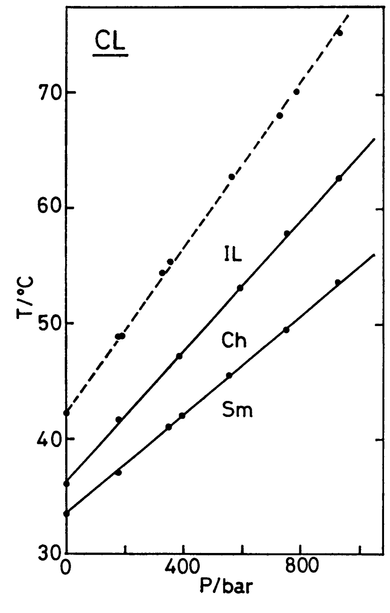

Fig. 4. Phase diagram of cholesteryl linoleate.
--: So-IL transition.

$$(dT/dP)_{\text{Sm-Ch}} < (dT/dP)_{\text{Ch-IL}}[<(dT/dP)_{\text{So-IL}}].$$

In other words, the temperature range over which the liquid crystalline phases are stable is widened by the application of pressure. The trend found often experimentally is predicted by the order-disorder transition theories based on a lattice model.[14–16]

The volume changes ΔV at 1 bar accompanying the transitions are computed by putting the slopes (dT/dP) and the literature values[9] of the enthalpy changes ΔH into Clapeyron's equation,

$$\Delta V = \Delta H T^{-1}(dT/dP). \qquad (1)$$

The values of ΔV computed thus are listed in the last column of Table 1. The volume change for the

TABLE 1. THERMODYNAMIC DATA RELATED TO THE PHASE TRANSITIONS AT 1 bar

Compound	Transition	Transition point[a)] °C	ΔH[a)] kJ mol^{-1}	$\mathrm{d}T/\mathrm{d}P$ K kbar^{-1}	ΔV cm^3 mol^{-1}
Cholesteryl oleate	Ch-IL	48.5 (46.4)	0.491	32	0.49
	Sm-Ch	43.0 (41.8)	1.01	23	0.73
Cholesteryl linoleate	So-IL	42.3 (42.6)	29.9	36	34
	Ch-IL	36.3 (35.1)	0.543	28	0.50
	Sm-Ch	33.6 (34.0)	1.47	21	1.0
Cholesteryl linolenate	Ch-IL	38.0 (34.8)	0.433	30	0.42
	Sm-Ch	30.6 (33.0)	1.84	22	1.3

a) The transition points in the parentheses and enthalpy changes are from Ref. 9.

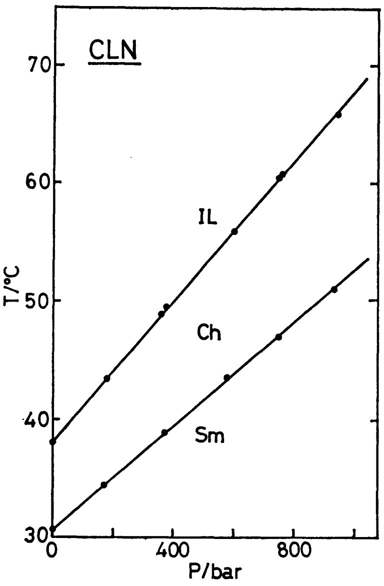

Fig. 5. Phase diagram of cholesteryl linolenate.

So–IL transition in CL is much larger than that for the Sm–Ch or Ch–IL transition, because in the former transition, the positional and rotational orders inherent in the solid state are completely lost at the same time. The ratio of the volume changes, $\Delta V_{\mathrm{Sm-Ch}}/\Delta V_{\mathrm{Ch-IL}}$ is larger than unity in every case, and increases as the molecular shape deviates further from rod-likeness. The former tendency indicates that one translational freedom brings about a larger volume change than two rotational freedoms. The volume change for the Sm–Ch transition increases with the number of the double bonds, while that for the Ch–IL transition is little affected. The volume changes for the Sm–Ch transition can be linearly correlated to the corresponding entropy changes in the homologous series, because the slopes ($\mathrm{d}T/\mathrm{d}P$) in Eq. 1 are all in the narrow range of 21 to 23 K kbar^{-1}.

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